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OFFICE OF NAVAL RESEARCH

END OF YEAR REPORT

June 1989-May 1990

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

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Submitted May 21, 1990

PART I

a. Papers Submitted to Refereed Journals

1) Gedridge, Jr., R. W.; Higa, K. T.; Nissan, R. A. *"Synthesis and Mechanistic Studies of Symmetric Tetraorganyltellurium(IV) (R_4Te) and Diorganyltellurium(II) (R'_2Te) Compounds (R = R' = Me, n-Bu, Me_3SiCH_2, and CH_2=CH; R'_2Te) Compounds (R = t-Bu and allyl)"* **Submitted to Organometallics (April 1990).**

b. Papers Published in Refereed Journals

1) Higa, K. T.; Harris, D. C. *"Synthesis and Characterization of Diallyl Telluride and Allyl Methyl Telluride"* **Organometallics,** 1989, 8, 1674.

2) Gedridge, R. W.; Higa, K. T.; Harris, D. C.; Nissan, R. A.; Nadler, M. P. *"Synthesis and Spectral Properties of Bis(alkyltelluro)ethynes, RTeC≡CTeR (R = Me, Et)"* **Organometallics,** 1989, 8, 2812.

3) Gedridge, R. W.; Harris, D. C.; Higa, K. T.; Nissan, R. A. *"Isolation and Characterization of Tetramethyltellurium(IV)"* **Organometallics,** 1989, 8, 2817.

4) Higa, K. T. *"$(t\text{-}Bu)_2GaAs(t\text{-}Bu)_2$: A Volatile Monomeric Arsinogallane""* **Organometallics,** 1990, 9, 275.

c. Books Submitted for Publication- **None**

d. Books Published- **None**

e. Technical Reports Published- **None**

f. Patents Filed- **3**

1) Tetra(Organyl) Tellurium Compounds and Process for Preparing Same (Navy Case No. 72204-Jan. 1990)

2) Monomeric Organometallic Compounds and Method of Preparing Same (Navy Case No. 72205- Jan. 1990)

3)Synthesis of Disodium Telluride (Navy Case No. 70645-Mar. 1990)

g. Patents Granted **None**

h. Invited Presentations at Topical or Society Conferences- **None**

i. Contributed Presentations at Topical or Scientific/Technical Society Conferences- **4**

1) Gedridge, R. W.; Harris, D. C.; Higa, K. T.; Nissan, R. A. ACS National Meeting, Miami, Sept. 1989.

2) Kirss, R. U.; Brown, D. W.; Higa, K. T.; Gedridge, R. W. ACS National Meeting, Miami, Sept. 1989.

3) Higa, K. T. ACS National Meeting, Miami, Sept. 1989.

4) Wells, R. L.; Higa, K. T.; McPhail, A. T.; Purdy, A. P. ACS National Meeting, Boston, April 1990.

j. Honors/Awards/Prizes- **None**

k. Number of Graduate Students Receiving at Least 25% Support on ONR Grant or Contract- **None**

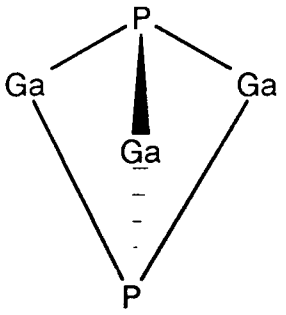
l. Number of Postdoctoral Fellows Receiving at least 25% Support on ONR Grant or Contract **None**

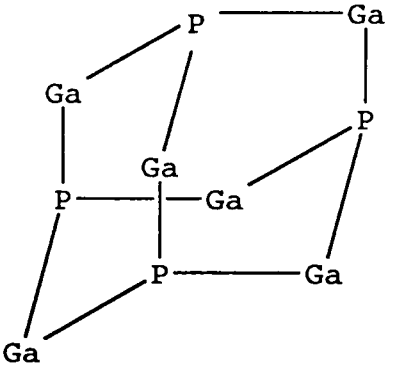
m. Other Funding

Principal Investigator: **Dr.. Kelvin T. Higa**
Telephone No. **(619) 939-1656 Autovon 437-1649**
ONR Scientific Officer: **Dr.. Harold E. Guard**

Project: New synthetic methods and techniques are being investigated to produce new organometallic compounds as precursors for optical and electronic materials. New synthetic routes for the preparation of III-V clusters and polymers and their electronic and optical properties are under investigation. The relationship between precursor structure and the resulting inorganic phases after pyrolysis are under examination to determine if certain cluster types will result in exclusively cubic or tetragonal structures after pyrolysis. Polymers may also yield III-V fibers under controlled pyrolytic conditions.

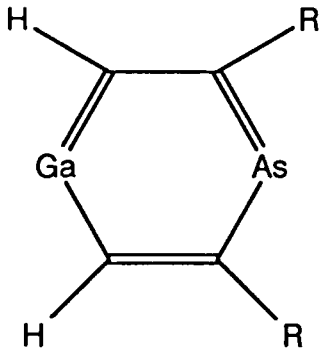
Significant Results: The first volatile monomeric III-V compounds of the type, $(t\text{-}Bu)_2M\text{-}E(t\text{-}Bu)_2$ (where M=Al, Ga, In and E=P,As) have been prepared and characterized. Pyrolysis of $(t\text{-}Bu)_2Ga\text{-}E(t\text{-}Bu)_2$, E=P,As at 280-300°C resulted in the formation of red polymers, $[(t\text{-}Bu)Ga\text{-}E(t\text{-}Bu)]_n$ while at temperatures of 350-425°C resulted in polycrystalline GaE. A sample of $(t\text{-}Bu)_2Ga\text{-}As(t\text{-}Bu)_2$ has been sent to The University of Utah (Dr. Cohen and Stringfellow) for an epitaxial film growth study. GaAs films have been deposited on quartz and pyrex and attempts are being made to coat dome materials with GaAs at low temperatures using our new compounds. The III-V polymers are being examined as conductive polymers and as non-linear optical materials. The steric requirements needed for the stabilization of monomers of the type, $(t\text{-}Bu)_2Ga\text{-}ER_2$, has been determined. The dimeric compounds $[(t\text{-}Bu)_2Ga\text{-}As(i\text{-}Pr)_2]_2$, $[(t\text{-}Bu)_2Ga\text{-}As(Et)_2]_2$ and $[(t\text{-}Bu)_2Ga\text{-}P(Ph)_2]_2$ have been prepared. Ethyl and i-Propyl groups on arsenic are not sufficiently bulky to prevent dimerization while phenyl groups on phosphorous leads to a dimer in the solid state and a monomer in solution. Presumably, this is due to the phenyl groups rotating rapidly around the P-C bond in solution while in the solid state they are configured to minimize their steric bulk. The reaction of $R_2As\text{-}SiR_3$ with $R_2Al\text{-}H$ has been demonstrated to give $R_2Al\text{-}AsR_2$ and silane(silane elimination). The reaction of $(Me_3Si)_3P$ with $GaCl_3$ in THF yields two new clusters and two polymers. The clusters are believed to be $P_2(GaCl \bullet THF)_3$ and $P_4(GaCl \bullet THF)_6$:

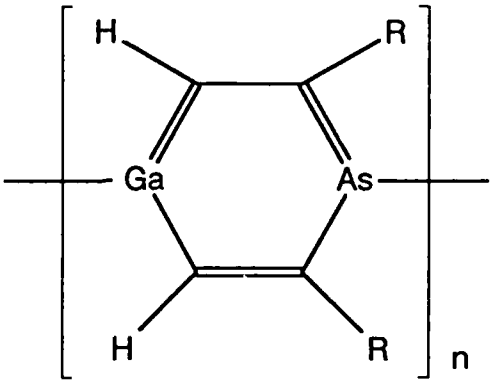




Attempts to crystallize these products are being pursued. A new synthesis involving the conversion of As_2O_3 to R_2AsCl , $RAsCl_2$ and R_3As has been established. This new synthesis should make the preparation of new arsines much easier and and also lead to higher yields.

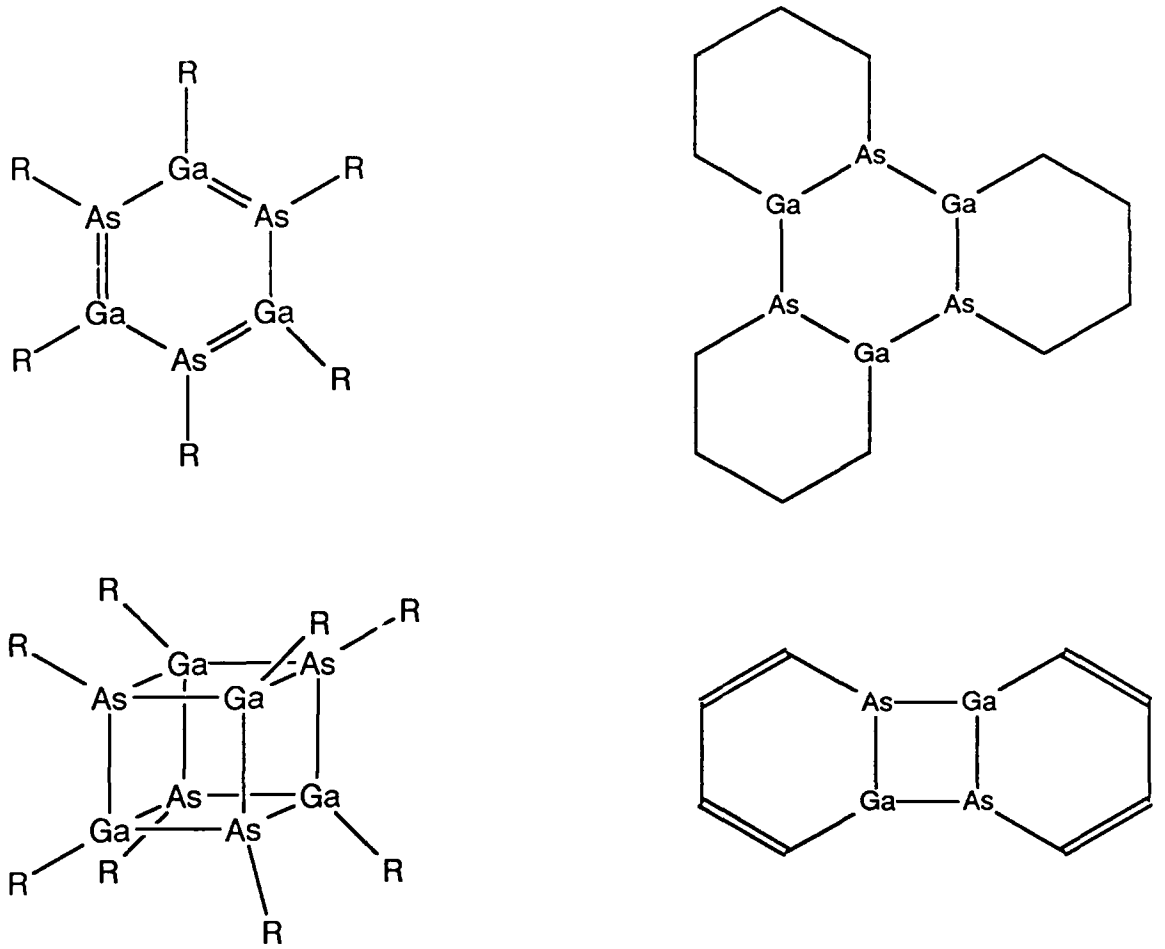
Future Plans: The utility of the III-V monomers in CVD systems will continue to be pursued by film growth studies. The preparation of new classes of III-V compounds both by new and established routes will continued. Once crystal structures of the new III-V clusters have been established by single crystal x-ray studies, pyrolytic studies will be initiated. The insertion reaction of arsines with $RGa(C{\equiv}CR)_2$ to form compounds of the type,





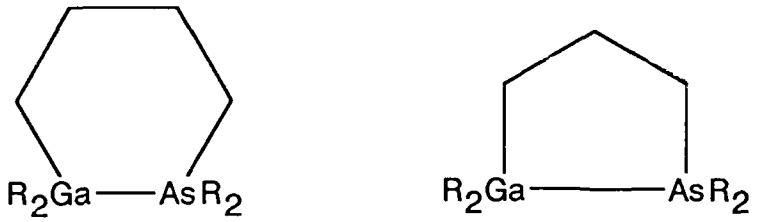
will be investigated. Other ring and caged III-V systems will be also be targeted (Figure 1):

Figure 1



Cyclic adducts (Figure 2) of III-V compounds will be prepared as possible precursors for CVD. The advantages of this type of compound, are that they significantly more air-stable than conventional source compounds, easily purified and they retain the III-V atom ratio at 1:1.

Figure 2



Dr. Kenneth Lee who got his PhD working with Prof. John Gladysz will be working on this project part-time as a postdoctoral fellow as of mid July. His position will be paid for by a related project.